

Melting of a flexible-chain polymer crystallized in a porous medium

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Abstract

The melting of a flexible-chain linear polymers, polyethylene oxide with $M = 40000$, introduced into porous substances with a pore diameter from 40 to 1440 Å, was investigated. Depending on the character of the melting, this range of pore diameters can be divided into two regions, whose boundary lies between 110 and 320 Å. In large pores, a high degree of crystallinity (≥ 0.7) was attained. The shape of melting curves was explained by the presence of two types of regions: the highly ordered and the relatively less ordered. In this case, the proportion of the less ordered regions was found to increase with overcooling upon the crystallization. In large pores, the dependence of the melting point lowering, $\Delta T(m)$, on the reciprocal pore diameter d was linear, as predicted by Gibbs-Thomson relation. It was shown that the melting point lowering was due to contributions from the lamellar and lateral surfaces of lamellar crystallite. In this case, lamellar crystallite probably occupied only a part of the cross-section of a pore. The rest of the cross-section was occupied with less ordered crystalline and/or amorphous regions. In smaller pores, the maximal degree of crystallinity was ≤ 0.3 . $\Delta T(m)(1/d)$ dependences deviated from the linear dependence obtained for wide pores. The lamellar surface was found not to contribute to the lowering of the melting point. Measurements of the transverse NMR relaxation showed that, in such pores, the motion in the crystalline phase was more intense. |

The melting of a flexible-chain linear polymer, polyethylene oxide with $M = 40\,000$, introduced into porous substances with a pore diameter from 40 to 1440 angstrom, was investigated. Depending on the character of the melting, this range of pore diameters can be divided into two regions, whose boundary lies between 110 and 320 angstrom. In large pores, a high degree of crystallinity (≥ 0.7) was attained. The shape of melting curves was explained by the presence of two types of regions: the highly ordered and the relatively less ordered. In this case, the proportion of the less ordered regions was found to increase with overcooling upon the crystallization. In large pores, the dependence of the melting point lowering, ΔT_m , on the reciprocal pore diameter d was linear, as predicted by Gibbs-Thomson relation. It was shown that the melting point lowering was due to contributions from the lamellar and lateral surfaces of lamellar crystallite. In this case, lamellar crystallite probably occupied only a part of the cross-section of a pore. The rest of the cross-section was occupied with less ordered crystalline and/or amorphous regions. In smaller pores, the maximal degree of crystallinity was ≤ 0.3 . $\Delta T_m(1/d)$ dependences deviated from the linear dependence obtained for wide pores. The lamellar surface was found not to contribute to the lowering of the melting point. Measurements of the transverse NMR relaxation showed that, in such pores, the motion in the crystalline phase was more intense.
